Using the N/C ratio to correct bulk radiocarbon ages from lake sediments: Insights from Chilean Patagonia

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Abstract

The offset between AMS radiocarbon ages obtained on bulk lake sediments and the true age of deposition was evaluated at four sites in Northern Chilean Patagonia. Our results show that the bulk radiocarbon ages are systematically older by 300 to 1100 years. In this region free of carbonate and carbonaceous rocks, we argue that this difference results from variable inputs of terrestrial organic carbon from the Holocene soils that cover the lake watersheds. For the four studied lakes, the age offset is clearly related to the fraction of terrestrial carbon preserved in the lake sediments, which was estimated using the N/C ratio of the bulk organic matter. We propose that N/C measurements can be used to significantly improve chronologies based on radiocarbon dating of bulk lake sediments.

Keywords: old carbon, age model, soil organic matter, chronology

1. Introduction

Lake sediments generally contain high resolution records of past climate and environmental change. In order to assess the amplitude of these changes and compare with other records at local, regional, and global scales, accurate sediment core chronologies are needed. In paleolimnology, absolute core chronologies are most frequently based on radiocarbon dating, which is ideally performed on well-preserved remains of terrestrial plants such as wood fragments, seeds and leaves (Törnqvist et al., 1992; Abbott and Stafford, 1996; Barnekow et al., 1998; Turney et al., 2000; Björck and Wohlfarth, 2001) or on organic compounds (biomarkers) derived from plants that utilize atmospheric CO_2 (Eglinton et al., 1997; Uchikawa et al., 2008; Hou et al., 2010). However, a large number of lake sediment core chronologies are still built on radiocarbon ages obtained on bulk sediment because (1) well-preserved remains of terrestrial organic matter are rare, and (2) compound-specific analyses are expensive and require large amounts of material.

In the literature, it is generally well accepted that radiocarbon ages obtained on the organic fraction of bulk sediment samples rarely reflect the true age of deposition (e.g., Björck and Wohlfarth, 2001). The underlying reason is that the bulk organic matter contains variable mixtures of (1) aquatic carbon produced in the water column and (2) terrestrial organic carbon, including plant debris, soil organic matter and debris of carbonaceous rocks such as shale, lignite and coal. Radiocarbon ages obtained on bulk sediment are therefore affected by (1) the hardwater effect, i.e. dilution of the ^{14}C concentration of aquatic organic matter by dissolved carbon originating from radiocarbon-dead calcareous rocks, and (2) incorporation of pre-aged terrestrial organic matter from soils and carbonaceous rocks in the lake watershed. Although the hardwater effect is relatively well understood (e.g., Andrée et al., 1986;

MacDonald et al., 1991; Barnerkow et al., 1998; Grimm et al., 2009), the processes involving transport and incorporation of soil organic matter in aquatic systems, and the effect of soil organic carbon on bulk radiocarbon ages in general, remains poorly constrained (e.g., Eglinton, 2010). The few authors that address the issue conclude that bulk radiocarbon ages are not accurate enough to provide reliable core chronologies (Björck and Håkansson, 1982; Björck et al., 1998; Abbott and Stafford, 1996) but they do not propose a method to correct ages obtained on such samples, although Björck and Håkansson (1982) noticed that the age difference is related to the amount of re-deposited pollen grains and inversely related to the total organic carbon content (TOC) of the sediment.

Here, we explore the possibility to estimate the effect of soil organic matter input on bulk radiocarbon ages, using four lake sediment cores from Chilean Patagonia. We deliberately selected lakes of different sizes, of different drainage basin/lake area ratios, and distributed across several hundreds of kilometers since our goal was to identify a method that is not lake-specific but that is at least valid at the regional scale

2. Material and study area

Four short (50-150 cm) sediment cores were collected in the deepest basins of small to mid-size (0.22 to 165 km^2) soft-water lakes in Northern Chilean Patagonia, using a short UWITEC gravity coring system, which preserves the water-sediment interface. The four lakes are roughly located along a North-South transect (Fig. 1), and their morphometrical characteristics are summarized in Table 1. The geological setting of the lake watersheds consists in various mixtures of volcanic, igneous and metamorphic rocks devoid of carbonate or carbonaceous deposits (Niemeyer et al., 1984; Sernageomin, 2003). The bedrock of the lake watersheds is covered by post-glacial volcanic soils of variable thickness (Bertrand and Fagel, 2008; Gut, 2008). These soils are acid and free of carbonates (Bertrand and Fagel, 2008; Ghazoui, 2011; Bertrand et al., 2012). These geological characteristics result in a negligible hardwater effect and in the lack of radiocarbon-dead organic carbon input. Precipitation in the area is generally high, with rates varying from 600 mm/yr at Thompson to 2200 mm/yr at Puyehue (New et al., 2002).

Insert figure 1 and table 1

3. Methods

Shortly after collection, the cores were split, described and continuously sub-sampled in 1 cm thick slices. Samples were then freeze-dried and homogenized in an agate mortar. In parallel, macroscopically visible remains of terrestrial plants were separated from the sediment and oven-dried at 40ºC.

Radiocarbon ages of thirteen bulk sediment samples and of three terrestrial macro-remains were determined at NOSAMS, USA (Table 2). Preparation of the bulk sediment samples consisted in acid pre-treatment only (McNichol et al., 1994). The pretreatment of the plant/wood samples involved the base extraction of humic and fulvic substances and acid removal of eventual inorganic carbon. All the samples were older than the bomb peak (Fm<1), and the radiocarbon ages were calibrated with OxCal 4.0, using the SHCal04 calibration curve of McCormac et al. (2004). Ages obtained on fragile remains of terrestrial plants, such as leaves and twigs, are considered to represent the true age of deposition since they are not likely to withstand long periods of storage in a terrestrial setting. For PU-I core, no terrestrial remain was found, but we used two tephra layers independently-dated at 1921-22 AD (47.5 – 48 cm) and 1908 AD (53.5 – 54 cm; Bertrand et al., 2008).

Insert table 2

The sediment samples were analyzed for TOC and TN/TOC (hereafter N/C) at the UCDavis Stable Isotope Facility, after pretreatment with 1N sulphurous acid in tin capsules.

Analytical details and instrument precision are given in Bertrand et al. (2010). The fraction of terrestrial carbon (f_T) was estimated from the N/C ratios of the bulk sediment samples, following Perdue and Koprivnjak (2007) and Bertrand et al. (2010). This implies using the following equation:

$$f_T = \frac{(N/C) - (N/C)_A}{(N/C)_T - (N/C)_A} \qquad (1)$$

where $(N/C)_A$ and $(N/C)_T$ represent the N/C ratios of the aquatic and terrestrial end-members, respectively. An N/C value of 0.069 (C/N = 7.7) was used for the aquatic end-member following Bertrand et al. (2010), and a value of 0.055 (C/N = 18) was used for the terrestrial end-member. The latter takes into account a mixture of soil organic matter (C/N = 15-18) with low amounts of fresh or degraded plant remains (C/N = 30-100).

4. Results and discussion

Results of radiocarbon measurements are summarized in Table 2 and represented in Figure 2. In the four analyzed sediment cores, the radiocarbon ages obtained on bulk sediment are in stratigraphic order but they are systematically older than radiocarbon ages obtained on terrestrial macrofossils or than independently-dated tephra layers (Fig. 2). It is also clear that the x-intercepts of the age-depth curves that fit through the weighted averages of the bulk radiocarbon ages are much older than the year of core collection (Fig. 2), indicating that the ages obtained on bulk sediment are older than the true age of deposition. The age offset between the age-depth curves and the weighted averages of the radiocarbon ages obtained on terrestrial macro-remains (or the 1908 AD tephra for Puyehue) is between 286 (Thompson) and 870 (Burgos) years. These results are similar to what Barnekow et al. (1998) and Björck et al. (1998) observed in Swedish lakes, where the age difference was explained by the hardwater effect and/or input of old and reworked soil organic material. Similar results were also obtained on Arctic lakes (Abbott and Stafford, 1996), where the radiocarbon age of the modern sediment-water interface was ~1000 years too old. For our four studied lakes, the hardwater effect is negligible, and we attribute the age difference to an input of old carbon previously stored in the post-glacial volcanic soils. This interpretation is further supported by radiocarbon measurements obtained on modern river sediment samples from the watershed of Lago Puyehue (Table 2), which display radiocarbon concentrations lower than the contemporaneous atmospheric concentration (Fm=1.081 in 2001; Hua and Barbetti, 2004). This indicates that our river samples are composed of a mixture of pre-bomb carbon, most likely from soils, and contemporaneous organic matter. These results are in agreement with Eglinton (2010), who demonstrates that delivery of terrestrial organic carbon to sedimentary environments through river transport may take several hundred to thousand years.

Insert figure 2

In order to construct realistic age models for cores Trapial, Burgos and Thompson, the age offset calculated above was subtracted from the age-depth curves fitting through bulk radiocarbon ages. For the three cores, the difference between the x-intercept of the corrected age-depth curves and the year of core collection was within error of the radiocarbon age obtained on terrestrial macro-remains, which validates our correction method. The age models were then fine-tuned by shifting the age-depth curves further to pass through the true x-intercept (i.e., the year of core collection). This resulted in final age offsets of 307 to 1080 years (Fig. 2). For the Puyehue core, the final age offset was simply calculated as the difference between the average of the 2 radiocarbon dates and the true age of the tephra layer immediately overlying them (Fig. 2).

The age offsets were then compared to several morphometrical, and sedimentological/geochemical parameters, and our results showed no significant relation between the age offsets and the drainage basin/lake area ratio (r=0.67, p=0.33) or precipitation rates (r=0.06, p=0.94). Likewise, age offsets are not significantly correlated with TOC (r=0.51, p=0.49), in contrast to what Björck and Håkansson (1982) observed in lakes from Southern Sweden. Our results however show a clear positive relation between the age offsets and the fraction of terrestrial organic carbon (Fig. 3), which reflects the terrestrial input of pre-aged organic carbon from the soils in the lake watersheds. This relation is clear when using the N/C (or f_T) values of (a) the core tops (0-1 cm), (b) the sediment sample corresponding to the depth of the terrestrial macro-remain or tephra used to calculate the offset, and (c) the entire core (Fig 3). The relations follow power or logarithmic laws with coefficients of determination (r^2) > 0.99 and > 0.96, respectively. This non-linear trend can be partly explained by the mixing between 2 sources of different radiocarbon ages (see, e.g., Ohkouchi and Eglinton, 2008).

The results presented in Figure 3 therefore suggest that the bulk organic matter of the four studied lakes is composed of a mixture of contemporaneous aquatic carbon with 1000-1200 years old carbon stored in soils, which is in agreement with the Holocene age of soils in the region (Bertrand and Fagel, 2008; Gut, 2008). More importantly, our results also suggest that N/C data can be used to estimate the age offset, and therefore correct radiocarbon ages obtained on bulk sediment. For lakes in Chilean Patagonia, the following equation, directly derived from the data presented in figure 3, can be used to calculate the age offset of any bulk sediment sample with known f_T (from N/C measurements):

$$\text{Age offset} = 169.26 * e^{(1.79 * fT)} \qquad (2)$$

Insert figure 3

The true age of deposition corresponding to a radiocarbon age obtained on a bulk lake sediment sample from Chilean Patagonia can therefore be calculated using the following equation:

$$\text{Age of deposition} = {}^{14}\text{C age} + 169.26 * e^{(1.79 * fT)} \qquad (3)$$

Whenever possible, age-depth models based on bulk radiocarbon ages corrected with this method should be validated using radiocarbon analysis of fragile remains of terrestrial organic matter from the same sediment core. Alternatively, methods such as ^{210}Pb dating and varve-counting could also be used to calculate the real age of deposition of pre-bomb levels selected for bulk radiocarbon dating.

For lake sediments outside Chilean Patagonia, the same principle applies, but because of differences in the age of soils, a new age offset-f_T equation has to be developed. A first-order estimate of the age offset can also be calculated using the following radiocarbon mixing equation (e.g., Okhouchi and Eglinton, 2008):

$$\Delta^{14}C_{bulk} = f_T * \Delta^{14}C_{soil} + (1 - f_T) * \Delta^{14}C_{aquatic} \qquad (4)$$

where Δ^{14}C represents the per mil deviation of the ^{14}C/^{12}C ratio for the sample relative to the ^{14}C/^{12}C ratio of the oxalic acid standard (Eglinton et al., 1997). The radiocarbon age is derived from Δ^{14}C using:

$$\text{age} = -8033 * \ln\,(1 + \Delta^{14}C/1000) \qquad (5)$$

This leads the following equation, which can be used to calculate the age offset of any sample with measured f_T, in an environment where the age of the soils is relatively well known.

$$e^{(\frac{-\,age\ offset}{8033})} - 1 = f_T * (e^{(\frac{-\,age\ soils}{8033})} - 1) \qquad (6)$$

which simplifies into:

$$\text{age offset} = -\,8033 * ln\left[1 - f_T + (f_T * e^{(\frac{-\,age\ soils}{8033})})\right] \qquad (7)$$

For the samples used in this study, the age offsets calculated using the above theoretical equation, and using a soil age of 1100 years, are correct within 88 years. This error appears acceptable given the large age errors that occur when no correction is applied.

One of the main advantages of the proposed method is that it can be applied downcore to provide a rapid assessment of the age offset of any radiocarbon age obtained on bulk sediment. It is applicable to sediment cores with high temporal changes in terrestrial carbon input, and it is therefore much more accurate than simply subtracting a single age offset for an entire core (see e.g., Barnekow et al., 1998). For the four studied cores, correcting the radiocarbon ages individually did not significantly improve the shape of the age-depth models since terrestrial supplies (i.e., N/C data) were fairly constant through time. A second advantage is that N/C measurements are relatively inexpensive, which makes this method applicable in routine. Other advantages are that it seems applicable to lakes of any size and that the age offset-N/C relations are valid for large regions, provided that the age of the soils remains relatively constant regionally.

A limitation of this approach is that it does not correct for the hardwater effect and it is therefore not applicable to lakes located in carbonate-rich settings. Also, on larger time-scales, the age offset is expected to vary downcore, independently of changes in terrestrial inputs, since the radiocarbon age of soils available for erosion varies with time. This issue can however be minimized by dating paired samples (i.e., bulk sediment and terrestrial macro-remain) at several stratigraphic levels downcore, and recalculating the age offset-N/C relation for different time-windows. Finally, the calculation of f_T using N/C data requires well-defined aquatic and terrestrial end-members. Selecting a reliable N/C value for the terrestrial end-member is generally complicated by the constant increase in N/C during degradation of terrestrial organic matter by incorporation into soils and transport by rivers (e.g., Bertrand et al., 2010). Extensive analysis of organic samples from the lake watersheds is therefore required to obtain an accurate N/C value for the terrestrial end-member. Similar problems may occur when trying to define the aquatic end-member since aquatic N/C values vary with nutrient availability and with plankton species-specific characteristics (Sterner and Elser, 2002).

One assumption that was made in this study is the equilibrium between lake water dissolved inorganic carbon (DIC) and atmospheric CO_2. In addition to the hardwater effect mentioned above, which is negligible in Chilean Patagonia, the radiocarbon age of DIC that is used by lake plankton also depends on (1) the potential sealing of an old water mass by lake ice or strong annual lake stratification, (2) the input of old water from a glacier, and (3) volcanic activity (e.g., Björck and Wohlfarth, 2001). The first two possibilities can be discarded because the studied lakes are well mixed in winter (Campos et al., 1989; Soto, 2002), they are not ice covered over long periods of time, and there is no glacier in their watersheds. Volcanic activity, however, is relatively important in the watershed of Lake Puyehue (the Puyehue-Cordon de Caulle volcanic complex - PCCVC - is located ~25 km to the northeast of the lake). Although some authors have shown that large springs in volcanically active regions may be depleted in ^{14}C (Rose and Davisson, 1996), there is currently no comprehensive study of the effects of juvenile volcanic carbon on lake water DIC. Given the importance of air-water CO_2 exchange in rivers (Raymond et al., 2004) and the efficient mixing of the studied lakes (Campos et al., 1989; Soto, 2002), the chances that the PCCVC is responsible for the presence of a ^{14}C-depleted DIC pool in Lake Puyehue are slim. This should however be tested by measuring $DI^{14}C$ of lake waters before, during and after a volcanic eruption.

Ultimately, our approach offers the potential to improve the chronology of lake sediment records where other accurate chronological techniques, such as varve-counting, tephrochronology or radiocarbon-dating of terrestrial macro-remains, are not applicable. We expect that the proposed age offset calculation equation will be valid for most Late Holocene lake sediment cores in Chilean Patagonia since the origin and nature of soils in the region is relatively uniform (Bertrand and Fagel, 2008). Although our present study is limited to lakes from Northern Chilean Patagonia, the age offset calculation approach presented here is applicable to lakes in other regions after calculation of the age offset – N/C relation using several paired samples with clearly distinct terrestrial carbon contents.

5. Conclusions

Our study confirms that radiocarbon ages obtained on bulk sediment samples are systematically too old, due to variable inputs of pre-aged terrestrial organic matter from soils in the lake watersheds. Our results also demonstrate a clear link between the fraction of terrestrial carbon, based on N/C measurements, and the age offset, which reveals the potential of N/C measurements to correct radiocarbon ages obtained on bulk sediment samples. The obtained relation offers the possibility to use inexpensive N/C measurements to significantly improve sediment core chronologies from lakes in Chilean Patagonia. For other regions, a similar relation may easily be calculated using N/C data and paired-radiocarbon measurements on pre-bomb samples from several lakes. Future work should focus on testing the proposed technique downcore and assess the number of paired samples necessary to calculate changes in age offset through time.

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Table 1

Location and characteristics of the four lakes and sediment cores used in this study. A_0: lake surface area; A_D: drainage area; Z_{max}: maximum depth. [1]: Plus two independently-dated tephra layers. [2]: From Bertrand et al (2008).

Lake	Year of sampling	A_0 (km^2)	A_d (km^2)	A_d/A_0	Z_{max} (m)	Core name	Core Location	Core length (cm)	Core depth (m)	# of radiocarbon dates
Trapial	2008	1.13	9.50	8.40	25	Trapial08-F	46.71364 °S 72.69969 °W	144	24	5
Burgos	2007	0.22	4.72	21.45	31	Burgos07	45.70947 °S 72.21492 °W	132	30	4
Thompson	2008	1.19	15.43	12.97	16	Thompson08-E	45.64075 °S 71.78528 °W	131	15	5
Puyehue	2002	165.4	1510	9.13	123	PU-I-P1	40.66277 °S 72.36925 °W	63	122	2 [1,2]

Table 2

AMS radiocarbon ages obtained on bulk sediment, leaf, twig and wood samples. Radiocarbon results were calibrated with OxCal 4.0, using the SHCal04 calibration curve (McCormac et al. 2004). Calibrated ages are at the 95.4% confidence interval. RS21 and RS34 correspond to river sediment samples from the watershed of Lake Puyehue (Rio Golgol and Rio Lican, respectively). For these samples, only the < 106 um fraction was used for analysis. Most of the samples were analyzed at NOSAMS (laboratory no. starting with OS), except for the Puyehue lake sediment samples that were measured at the Poznan Radiocarbon Laboratory (Poz-) or at Beta Analytics (Beta-). n.m.: not measured

Sediment core	Depth (cm)	Description	Laboratory no.	$\delta^{13}C$	F modern	14C age ± 1 σ	Calibrated age (years AD/BC)	Weighted average
Trapial 08F	62-63	bulk lake sediment	OS-69045	-29.05	0.657	3380 ± 35	BC 1730-1505	BC 1603
Trapial 08F	65-66	thin wood remain	OS-69032	-25.74	0.694	2930 ± 30	BC 1195-925	BC 1055
Trapial 08F	101-102	bulk lake sediment	OS-69046	-28.51	0.560	4660 ± 40	BC 3520-3110	BC 3374
Trapial 08F	139-140	bulk lake sediment	OS-69047	-28.40	0.476	5970 ± 40	BC 4930-4690	BC 4790
Trapial 08F	142-143	bulk lake sediment	OS-69117	-28.34	0.467	6120 ± 35	BC 5205-4840	BC 4973
Thompson 08E	33-34	bulk lake sediment	OS-79259	-28.29	0.957	350 ± 25	AD 1495-1640	AD 1562
Thompson 08E	68-69	bulk lake sediment	OS-69070	-28.89	0.920	670 ± 40	AD 1290-1400	AD 1346
Thompson 08E	96-97	bulk lake sediment	OS-69085	-28.41	0.904	810 ± 35	AD 1210-1295	AD 1252
Thompson 08E	122-123	twig	OS-68923	-27.68	0.892	920 ± 30	AD 1045-1225	AD 1160
Thompson 08E	125-126	bulk lake sediment	OS-69079	-28.66	0.850	1300 ± 40	AD 675-880	AD 773
Burgos 07	24.5	leaf	OS-68924	-30.04	0.989	90 ± 30	AD 1695-1950	AD 1854
Burgos 07	68-69	bulk lake sediment	OS-69089	-28.98	0.851	1290 ± 30	AD 685-880	AD 782
Burgos 07	97-98	bulk lake sediment	OS-69090	-28.84	0.839	1410 ± 30	AD 615-770	AD 673
Burgos 07	114-115	bulk lake sediment	OS-69118	-29.02	0.829	1510 ± 30	AD 555-650	AD 605
Puyehue PU-I-P1	54-54.5	bulk lake sediment	Poz-16436	n.m.	0.923	640 ± 30	AD 1300-1410	AD 1354
Puyehue PU-I-P1	55-55.5	bulk lake sediment	Beta-213316	-27.9	0.936	530 ± 40	AD 1395-1460	AD 1428
Puyehue RS21	Rio Golgol	bulk river sediment	OS-69037	-26.97	0.969	250 ± 40	AD 1515-1955	AD 1726
Puyehue RS34	Rio Lican	bulk river sediment	OS-69038	-27.82	1.027	--	--	--

Figure captions

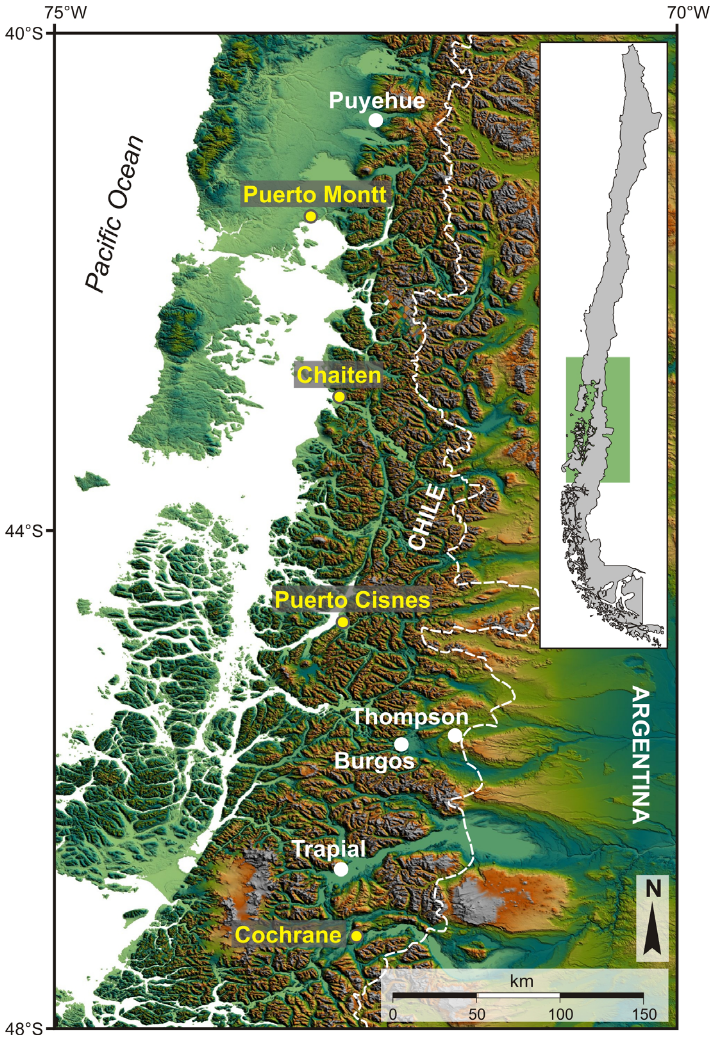
Figure 1 – Location of the studied lakes (labeled in white) in Northern Chilean Patagonia.

Figure 2 – Radiocarbon ages and age models. The dashed age-depth curves are based on the bulk radiocarbon ages only. The dashed arrow in (d) indicates different interpretations for the base of the 1960 earthquake deposit (see discussion in Moernaut et al., 2007).

Figure 3 – Relation between the fraction of terrestrial carbon (f_T) and the radiocarbon age offset. The error bar of the core average data represents 1 s.d. The term 'true age' depth refers to the depth of the terrestrial macro-remain or tephra used to calculate the offset. N/C values are systematically higher for the core top samples, which tends to demonstrate higher lake productivity during the last decade(s), likely due to a tendency towards lake euthrophication.

395 **Figures**

396



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399 Bertrand et al – Figure 1

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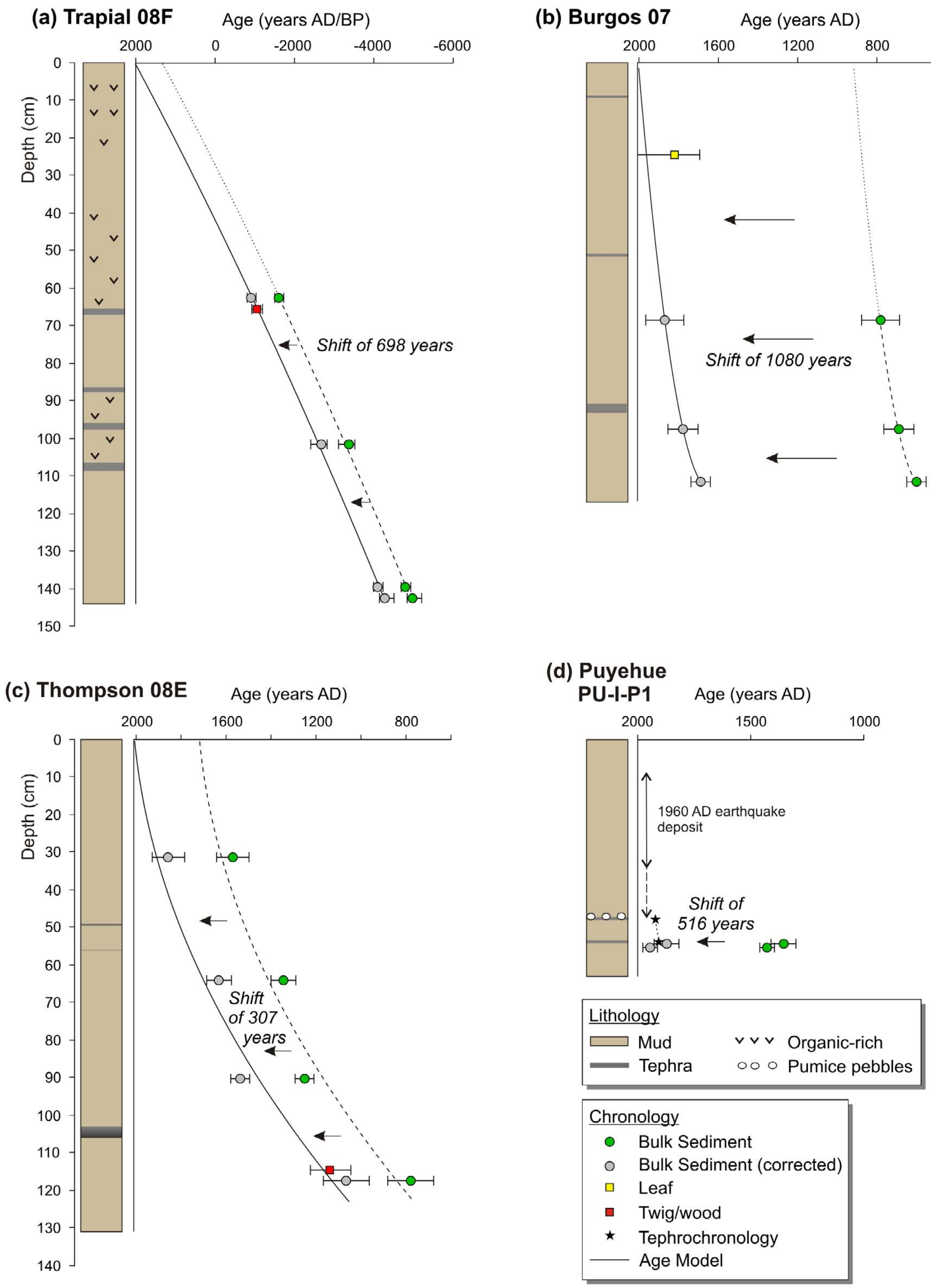

Bertrand et al – Figure 2

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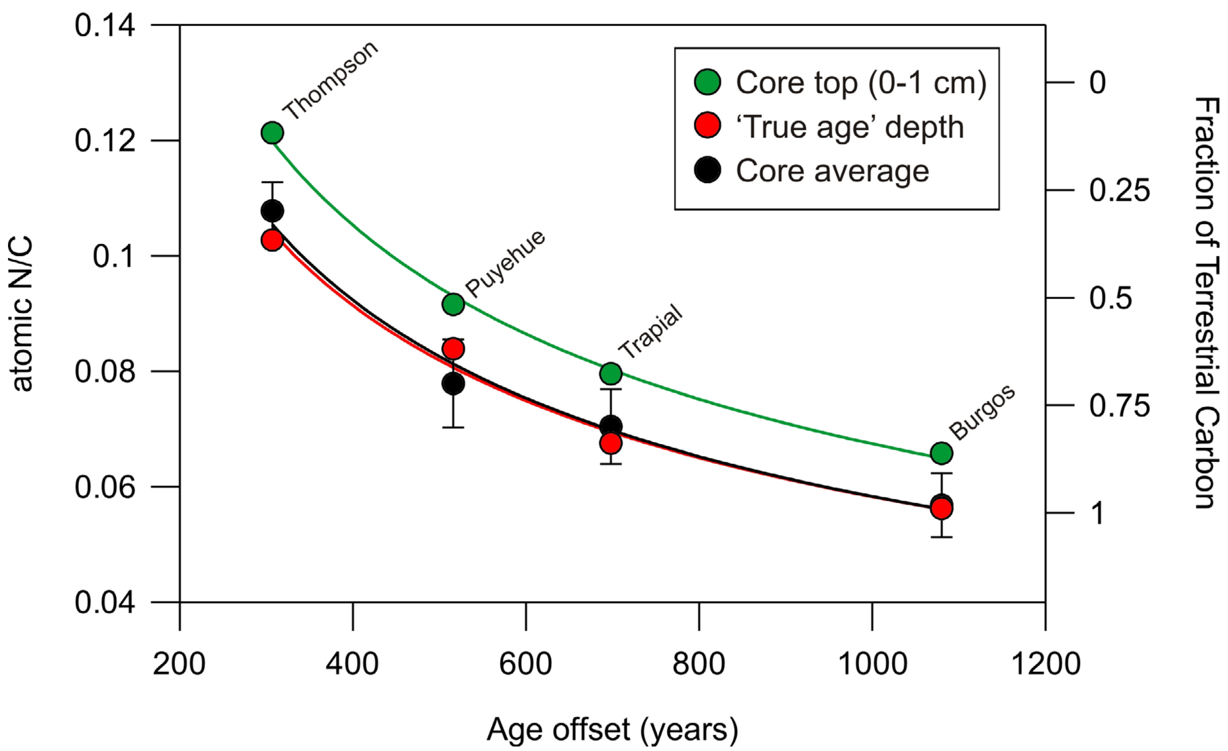

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407 Bertrand et al – Figure 3